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PHOSPHINE EVOLUTION CONTROL
IN RED PHOSPHORUS MUNITIONS

Pascal A. Tarantino
William L. Brown

RESEARCH DIRECTORATE

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Aberdeen Proving Ground, Maryland 21010-5423

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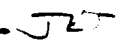Approved for public release; distribution is unlimited.

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Several desiccants and sorbents were investigated for reducing or eliminating corrosion in red phosphorus munitions. It was shown that corrosion will not occur in the absence of moisture. Moist air and phosphine from oxyacids corrode the electrical components of the munition. Aluminium silicate clay was found to be a very effective desiccant for moisture, and activated carbon was found to be an excellent sorbent for phosphine. The use of packets of desiccant and sorbent in a perfectly sealed munition round or carrying case will provide a non-corrosive environment.

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phosphine capacity

PREFACE

The work described in this report was authorized under Project
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in December 1987. The experimental data are recorded in laboratory notebook
CSL-82-0033.

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PHOSPHINE EVOLUTION CONTROL IN RED PHOSPHORUS MUNITIONS

1.   INTRODUCTION

Red phosphorus (RP) smoke munition, on long term storage, shows evidence of internal corrosion due to the degradation products of RP. When RP is exposed to normal atmosphere, it interacts with the moisture and oxygen of the air resulting in a gradual formation of phosphine (PH_3) and phosphorus oxyacids. The PH_3 further reacts with moist air to form more oxyacids. The phosphorus oxyacids corrode the electrical components of the RP smoke munitions and as a result, lowers their effectiveness.

This study was encouraged as a result of the "Proceedings of the 1986 Red Phosphorus Symposium" sponsored by the Munitions and Research Directorates of CRDEC[1]. The topics presented at this symposium dealt with the following areas: RP literature review from 1940 to the present, metal-phosphorus coordination, corrosion problems experienced with the smoke grenade and warhead rocket, sources of corrosion in the L8 grenade electrical contacts, RP stabilization, phosphine corrosion, and corrosion prevention related to RP.

The purpose of this study was to evaluate some solid desiccants and sorbents for the removal of moisture and PH_3 respectively from the chamber of the RP munition rounds. The evaluation of desiccants was based on the adsorption rate and capacity of moist vapor.

The rate and capacity of the desiccants were determined by analyzing for the water content at periodic time intervals. The rate and capacity of the sorbents were determined by exposing the sorbents to PH_3. The PH_3 was monitored with a gas chromatograph equipped with a flame photometric detector (FPD).

Alumina silicate clay (Al-Si-Clay) was found to be the best desiccant, and activated carbons (AC's) and magnesium dioxide (MnO_2) were found to be good PH_3 sorbents. Mixtures of MnO_2 and cupric oxide were not found to be any better than that of MnO_2 alone.

Small packets or "tea bags" of a desiccant and sorbent may be placed at a convenient place in the RP munition round; but in order for the packets to be effective, the RP munition must be completely sealed from the surrounding atmosphere.

2.   EXPERIMENTAL PROCEDURES

2.1   Desiccants.

The water content of desiccants was determined by the loss in weight with heating. The desiccants were exposed to water vapor in a desiccator, sampled periodically, placed in platinum crucibles, dried at 200°C and the loss in weight before and after drying corresponded to the amount of water adsorbed at any given time.

2.2   Evolution of PH_3.

The evolution of PH_3 from RP was determined at room temperature and at 70°C with super saturated salt solutions of different relative humidities (RH).

2.3   Sorption of PH_3.

The sorption of PH_3 by a sorbent was conducted at room temperature. The rate of reaction was carried out in an excess of sorbent, and the phosphine capacity in an excess of PH_3.

2.4   Phosphine Reaction Chamber.

The evolution, rate and capacity of PH_3 were conducted in Mason jars whose lids were modified to hold a rubber septum for sampling the inside of the jar (Figure 1). The evacuation and filling of the jar was done in a desiccator via tygon tubing, connecting the cylinder of the gas being introduced (N_2 or PH_3), a manometer, a rubber balloon and a vacuum line. A schematic lay-out as to how the Mason jars were filled and evacuated is shown in Figure 2. Hereafter the Mason jar, lid and septum will be referred to as the reaction chamber.

2.5   Phosphine Monitoring.

The evolution of PH_3 from RP and the consumption of PH_3 by sorbents inside the reaction chamber were sampled with gastight syringe through the rubber septum. A given volume of the sampled environment inside the reaction chamber was analyzed for PH_3 concentration with a gas chromatograph.

The gas chromatograph was a Varian, Model 13400 equipped with an FPD. The gases and flow rates were: carrier gas was nitrogen at a flow rate of 30ml/min, compressed air at 126ml/min, and the column packing was ParapackQ, 80x100. The temperatures were 50°C for the column, 50°C for the injection port and 220°C for the FPD. A Varian integrator, Model 4270 was used for recording the output.

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Fig. 1. PHOSPHINE REACTION CHAMBER

SEPTUM

CAP

EXPOXIED GLASS
VEIL TOP

RING

LID

MASON JAR (1 PINT / 473 ml)

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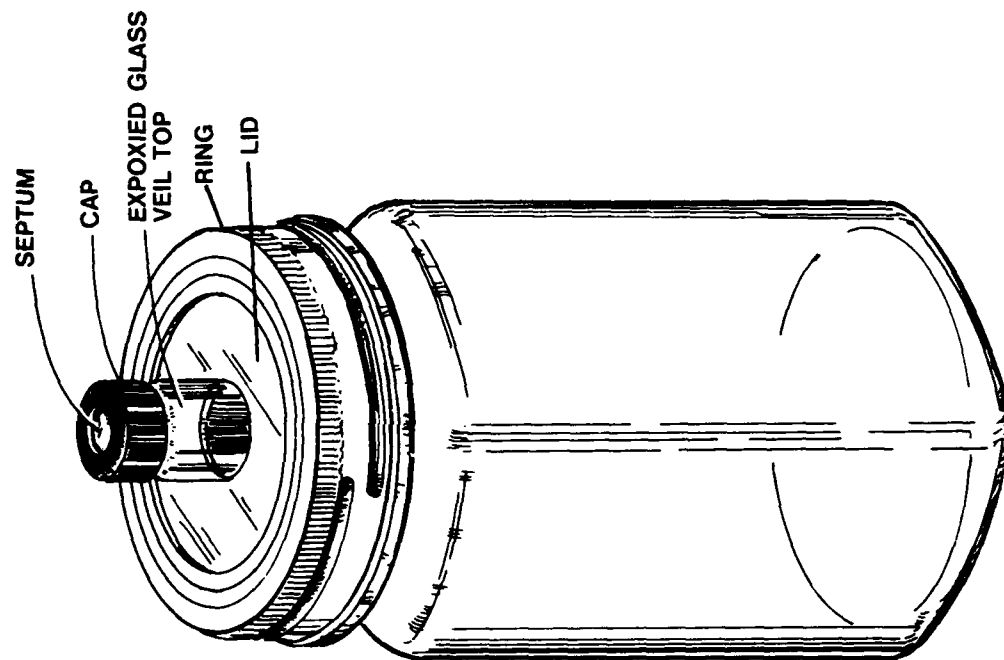
Fig. 2 SCHEMATIC LAYOUT FOR FILLING AND EVACUATING REACTION CHAMBER

N₂

PH₃

INSIDE OF HOOD

TO VACUUM

CLAMP

MANOMETER

HEAVY WALL TYGON TUBING

BALLOON

DESICCATOR WITH PH₃ REACTION CHAMBER
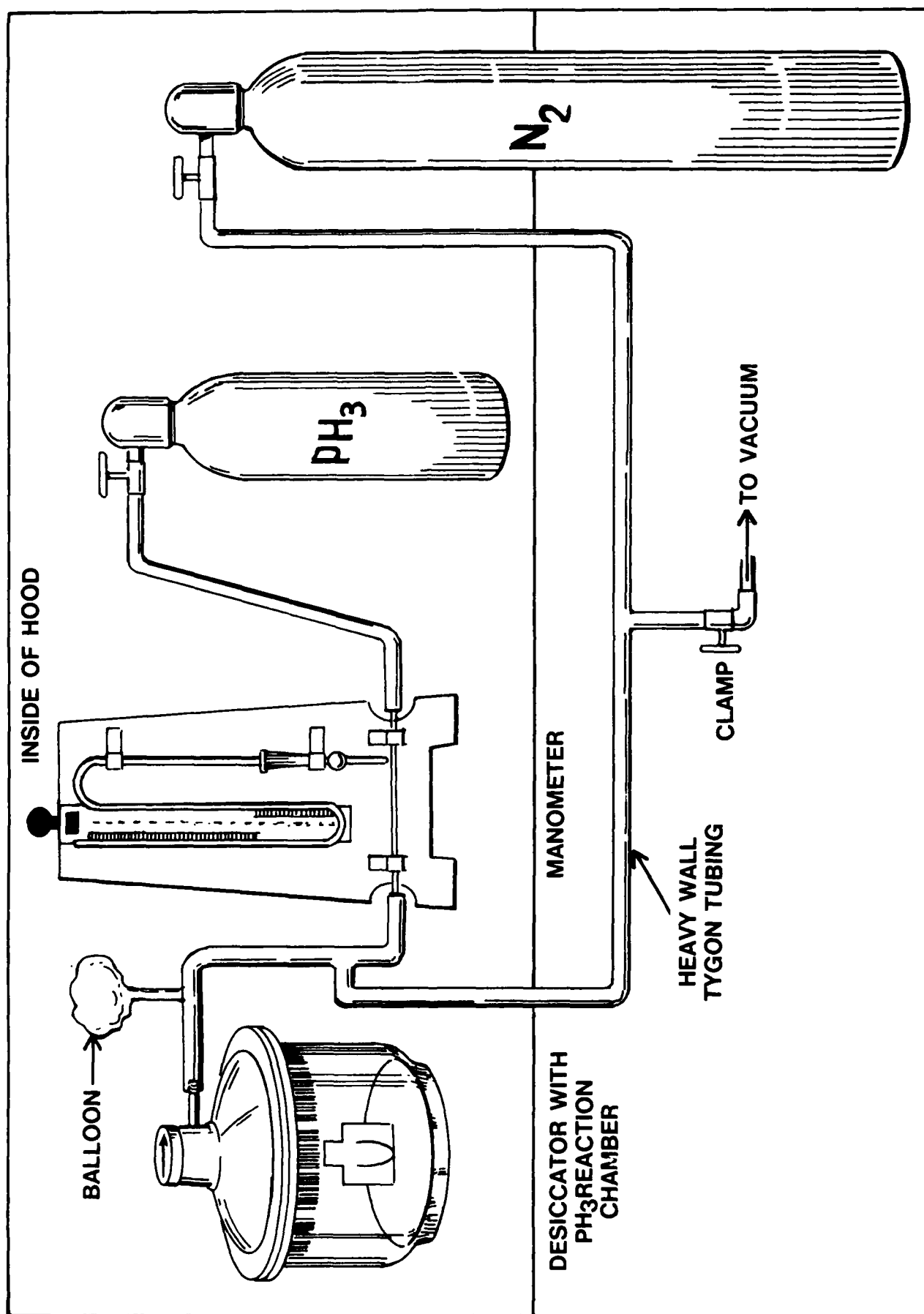
2.6   Chemicals Investigated.

2.6.1   Desiccants.

The desiccants investigated were lithium chloride (LiCl), calcium chloride ($CaCl_2$), magnesium perchlorate [$Mg(ClO_4)_2$], calcium sulfate ($CaSO_4$), silica gel, molecular sieves (3A, 4A, 5A and 13X) and alumina-silicate clay (Al-Si-Clay).

2.6.2   Red Phosphorus.

Three different types of RP were investigated. Two were from ERCO Industries; red amorphous phosphorus (RAP) and the corresponding stabilized red phosphorus (RAPS). The third was stabilized RP from Hoechst which was known as HB100S.

2.6.3   Sorbents.

2.6.3.1   Activated Carbons.

The activated carbons (AC) were supplied by three companies listed below: Anderson Development Co., Calgon Carbon Corp., and Sutcliffe Speakman Carbon Ltd. Anderson supplied three samples: Ax-21, Ax-31C, and Ax-31M; Calgon supplied one: BLP-4x10; and Sutcliffe supplied two samples: one impregnated with 0.01% silver nitrate and the other with 3% sodium dichromate. These carbons are currently in production and are readily available.

2.6.3.2   Metal Oxides.

Manganese dioxide and cupric oxide, and six mixtures of these two oxides were investigated.

3.   RESULTS

3.1   Desiccants.

The rate and capacity of desiccants were determined by exposing the desiccant to water vapor and periodically sampling for water content. The desiccants investigated as shown in Table 1 were four molecular sieves, two silica gels, four metal salts, and Al-Si-Clay.

The water capacities, after 92 hours, plateaued to 14-16% for the molecular sieves, 14-22% for the silica gels, 7-70% for the metal salts and 22-25% for the Al-Si-Clay. The metal salts, except $CaSO_4$, deliquesced at and after 92 hours.

Table 1
WATER ADSORPTION BY DESICCANTS WITH TIME

DESICCANT / HOURS	% WATER ADSORPTION (CAPACITY)								
	2	20	24	68	92	116	140	164	186
MOLECULAR SEIVES									
3A	3	10	13	13	16	15	15	15	17
4A	1	9	12	13	15	14	15	15	15
5A	1	6	11	11	14	13	14	13	16
13X	1	12	13	13	16	16	16	16	–
SILICA GEL									
28-200	5	10	13	14	16	20	21	21	21
16-65	1	5	8	9	14	16	20	22	22
METAL SALTS									
$CaCl_2$	8	10	17	26	38	42[a]	52[d]	57	63
$CaSO_4$	0.1	5	6	6	7	7	7	7	7
$Mg(ClO_4)_2$	0.1	7	11	16	29[a]	36[c]	43[d]	43	52
$LiCl_2$	3	11	18	27	35[b]	38[c]	57[d]	65	74
CLAY, ALUMINA-SILICATE	5	17	20	21	22	23	24	24	25

a = PASTY, b = WET, c = SLURRY, d = LIQUID

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Al-Si-Clay indicated a rapid initial water adsorption which levelled off at 24-25% after 116 hours exposure to water vapor. This desiccant turned out to be the most effective. It may be purchased in packets (3x3x1/8") known as Desi-Pack from United Desiccants, P.O. Box 105, Belen, NM 87002.

3.2   Evolution of PH$_3$ from RP.

The rate of PH$_3$ release from RP is a function of relative humidity (RH) and temperature. This was illustrated by exposing 10g of RAP at different humidities[2-4] and temperatures.

The RH was controlled by super saturated salt solutions which are given in Table 2. The RAP was exposed to salt solutions having 11, 27, 57, 85 and 100% RH at room temperature; and 11, 21, 72, 80 and 100% at 70°C. The quantities of PH$_3$ evolved at different temperatures are shown in Table 3.

This experiment was set up in reaction chambers that contained a vial with 25ml of super saturated solution, 10g RAP, evacuated, refilled with nitrogen and capped the reaction chamber with a septum. The reaction chambers were left half at room temperature and the other half in an oven at 70°C. The PH$_3$ concentration was measured after 24, 48, and 96 hours which gave a gradual increase with time but the increase from 24°C to 70°C was 30-50 fold.

3.3   Stability of RP.

The stability of RP is better in dry condition regardless of whether the RP is stabilized or not. This is clearly illustrated by the results in Table 4. Here the HB100S, RAPS and corresponding mixes are compared with HB100S. The RP samples were placed in a reaction chamber with air and 85% RH. A second set up was run in similar reaction chambers except that the reaction chambers were first evacuated and then refilled with dry nitrogen at atmospheric pressure. The degradation of RP in air and 85% RH was 29.3-114.5 greater for RAP than the HB100S. This gap increases with time. The stability in dry nitrogen and silica gel was much better. The RAP is only 1.6-6.9 times more degradable than the HB100S.

3.4   **Effect of Water Vapor and Activated Carbons on RAP Stability.**

Four samples were set up in reaction chambers each containing 10g RAP powder at room temperature. The first contained RAP only; the second, a source of water vapor; the third, 1g AC; and the fourth, water vapor and 1g AC. The results are given in Table 5. These reaction chambers were not evacuated, they were set up in normal atmosphere and capped with a septum. The PH$_3$ concentration increased with time as indicated by set up #1, set up #2 containing water vapor increased by a factor of 5-8, and set

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Table 2
SUPER SATURATED SALT SOLUTIONS
FOR RELATIVE HUMIDITY CONTROL

SUPER SATURATED SALT SOLUTION	RELATIVE HUMITIDY, %	
	25°C	70°C
LiCl	11.1 (a)	∿11 (a)
KF	27 (b)	21 (b)
NaBr	57.7 (a)	-
NaCl	-	75.1 (b)
KCl	84.3 (a)	80 (b)

(a) FROM R.H. STOKES AND ROBINSON
      IND. ENG. CHEM 41, 2013 (1949)

(b) FROM D.S. CARR AND B.L. HARRIS
      IND. ENG. CHEM 41, 2014 (1949)

Table 3
PHOSPHINE EVOLUTION FOR 10g RAP AS A FUNCTION OF RELATIVE HUMIDITY (RH) AND TEMPERATURE WITH TIME

A. AT ROOM TEMPERATURE

% RH/TIME	MICROGRAM OF PHOSPHINE EVOLVED		
	24 HRS	48 HRS	96 HRS
11	53	100	106
27	123	255	239
57	341	1072	1275
85	386	1185	1492
100	391	1207	1636

B. AT 70°C

% RH/TIME	24 HRS	48 HRS	96 HRS
11	2340	5858	–
21	6258	15291	–
72	9786	27240	–
80	10948	31750	–
100	11480	39623	–

Table 4
COMPARISON OF STABILIZED AND NON-STABILIZED RP SAMPLES IN MOIST AND DRY ENVIRONMENT WITH TIME

REACTIVE CHAMBER CONTAINED 1g SAMPLE AT ROOM TEMPERATURE

A. 85% RELATIVE HUMIDITY AND NORMAL AIR

| | TIME, HOURS | | | | | |
| SAMPLE | 24 | | 48 | | 144 | |
	PH_3 (ug)	RR*	PH_3 (ug)	RR*	PH_3 (ug)	RR*
HB100S	2.3	1.0	2.8	1.0	3.2	1.0
HB100S - MIX	4.6	2.0	7.0	3.1	8.1	2.6
RAPS	0.7	0.3	2.2	0.8	6.9	2.2
RAPS - MIX	1.8	0.8	2.8	1.0	7.9	2.5
RAP	65.8	29.3	116.6	41.2	362.0	114.5

B. DRY NITROGEN AND SILICA GEL

SAMPLE	PH_3 (ug)	RR*	PH_3 (ug)	RR*	PH_3 (ug)	RR*
HB100S	0.44	1.0	0.56	1.0	0.82	1.0
HB100S - MIX	NONE		NONE		NONE	
RAPS	NONE		NONE		NONE	
RAPS - MIX	NONE		NONE		NONE	
RAP	0.68	1.6	1.68	3.0	5.6	6.9

*RELATIVE RATIO

Table 5
EFFECT OF WATER VAPOR (H_2O) AND ACTIVATED CARBON (AC) ON RAP AT ROOM TEMPERATURE

TIME (HOURS)	SAMPLE* CONDITIONS	PHOSPHINE EVOLVED (ug)
5	1	85
	2	343
	3	NONE
	4	NONE
96	1	155
	2	704
	3	NONE
	4	NONE
120	1	326
	2	1662
	3	1
	4	1
144	1	337
	2	2138
	3	2
	4	3

*MATERIAL PLACED IN REACTION CHAMBERS
1. 10g RAP
2. 10g RAP + H_2O
3. 10g RAP + 1g AC
4. 10g RAP + H_2O + 1g AC

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ups #3 and #4 had a negligible increase. This indicates that AC sorbs the PH_3 as it is being produced in #3 and #4.

3.5   Reaction Rate Constants of PH_3 for Desiccants and Sorbents.

The reaction rate constants of PH_3 with desiccants and sorbents were carried out in reaction chambers which contained 100mg solid desiccant or sorbent, evacuated and refilled the chamber with nitrogen. Sufficient 0.1% PH_3 was introduced to the nitrogen filled reaction chamber to give a PH_3 concentration of 200ppm by volume.

The ratio of reactants above was 100mg sample to 1.7 mg PH_3 or 59:1 which is more than adequate to meet the pseudo-first order reaction requirement. The PH_3 concentration inside the reaction chamber was sampled at convenient time intervals. The peak area output (A) of the gas chromatograph was plotted against time (t) according to the following equation[4]:

$$\ln[A] = \ln[A] - kt$$

A plot $\ln[A]$ against t gave a straight line whose slope was equal to the rate constant, k, in reciprocal minutes. Since the rate constant is independent of concentration, the $\ln[A]$ versus time, t, was used to calculate k. The half life of the reaction was calculated using the following relationship:

$$t1/2 = 0.693/k$$

which is the time for half of the reaction to be completed. The experimental rate constant and the calculated half life for metal salts, molecular sieves, metal oxides and AC's are given in Table 6. The desiccants were very slow reacting with PH_3 while the sorbents are relatively faster. Based on these results only the sorbents will be further investigated later for PH_3 capacity.

3.6   Water Adsorption by Activated Carbon.

3.6.1   Water Content of AC as Received.

The AC's received from Anderson, Calgon, and Sutcliffe Speakman were dried at $200^\circ C$ overnight before they were used. Their water content varied from 0.6 - 62.4%. The amount of water present is dependent on shape, surface area, pore size and the humidity to which the AC's have been exposed. Some of these characteristics and the water content found in the AC's are presented in Table 7.

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Table 6
PHOSPHINE REACTION RATE CONSTANT (k), AND HALF LIFE (t ½), WITH DESICCANTS AND SORBENTS

A. DESICCANT (100mg)	k (min^{-1})	t ½ (min)
1. METAL SALTS		
$CaSO_4$	0.83×10^{-4}	8349
SILICA GEL	0.50×10^{-4}	14153
Al-Si-CLAY	0.85×10^{-4}	8153
$KMnO_4$	6.7×10^{-4}	1028
$K_2Cr_2O_7$	1.2×10^{-4}	5916
2. MOLECULAR SEIVES		
3A	4.0×10^{-4}	1733
4A	4.2×10^{-4}	1650
5A	1.0×10^{-4}	7134
13X	1.8×10^{-4}	3915
B. SORBENTS (100mg)		
1. METAL OXIDES		
MnO_2	27.0×10^{-2}	2.6
CuO	17.4×10^{-2}	4.0
MnO_2CuO		
10/1	17.0×10^{-2}	4.1
8/1	13.6×10^{-2}	5.1
6/1	19.2×10^{-2}	3.6
4/1	23.4×10^{-2}	3.0
2/1	9.6×10^{-2}	7.2
1/1	8.5×10^{-2}	8.2
2. ACTIVATED CARBON		
ANDERSON - 21 (POWDER)	10.9×10^{-2}	6.4
ANDERSON - 31C (PELLETS)	0.4×10^{-2}	173.0
ANDERSON - 31M (PELLETS)	0.4×10^{-2}	173.0
CALGON (GRANULES)	1.6×10^{-2}	43.6
SUTCLIFFE (Cr) (GRANULES)	1.8×10^{-2}	38.5
SUTCLIFFE (Ag) (GRANULES)	4.6	15.1

Table 7
CHARACTERISTICS OF ACTIVATED CARBONS AS RECEIVED FROM MANUFACTURER

ACTIVATED CARBON	FORM	SURFACE AREA (M^2/g)	WATER CONTENT FOUND (%)
ANDERSON – 21	POWDER	2800 – 3500	62.4
ANDERSON – 31 C	PELLETS		0.6
ANDERSON – 31 M	PELLETS		3.1
CALGON	GRANULES: 4x10	1050 – 1150	0.9
SUTCLIFFE (0.01 % Ag)	GRANULES: 8x16	1000 – 1100	11.8
SUTCLIFFE (3% Cr_2O_7)	GRANULES: 8x16		13.2

3.6.2 Dry AC's Exposed to Water Vapor.

Dry AC's were exposed to water vapor, under controlled conditions, in a desiccator. The AC's were sampled at convenient intervals for water content determination. MnO_2 and CuO were also treated in a similar manner. The results obtained are shown in Table 8. The three Anderson's samples, after 352 hours, gave about 49% water, Calgon 28%, MnO_2 22.7% and CuO was negligible.

3.7 Phosphine Capacity of Sorbents.

3.7.1 Dry Sorbents.

The phosphine sorbency of dry, solid sorbents was determined by reacting 1% PH_3 with a given weight of sorbent in a reaction chamber which was evacuated to about 70 mm of mercury. After the vacuum was shut off the PH_3 was introduced into the desiccator containing four reaction chambers until a positive pressure was indicated by the rubber balloon (see Figure 2). If the balloon did not collapse after the PH_3 valve was shut off, it was an indication that the reaction chambers were completely filled with 1% PH_3 at atmospheric pressure. Opened the desiccator and capped the reaction chambers with a rubber septum.

The filled reaction chambers were kept at room temperature for four days after which the interior of the reaction chambers were sampled and the PH_3 concentration determined by gas chromatography. A control was set up treating it the same way as for the sorbents. The depletion of PH_3 due to the sorption by the sorbents was related to the control for calculating the weight of the sorbed PH_3 by a given weight of the sorbent in question.

The desiccants listed in Table 1 were also subjected to the same treatment given above; but since the amount of PH_3 sorbed by them was in the order 5mg/g or less they are not reported. The PH_3 capacity for the AC's, MnO_2, CuO, and mixes of MnO_2/CuO are given in Table 9. The PH_3 capacity for Anderson-21 powder, with a surface area of 2800-3500M2/g, was greater than 998mg PH_3/g. It means that all of the PH_3 was consumed by 6.7mg sample before or at 96 hours. The next two Anderson-31C and 31M had a PH_3 capacity of 475 and 367 respectively. These are both pellets on an adhesive support which lowers their surface area, thus giving lower capacities.

Calgon, granular with a 4x10 mesh and a surface area of 1050-1150 M2/g, had the next best PH_3 capacity of 978mg PH_3/g. The granules were all carbon with no support. The next best were Sutcliffe Speakman with capacities of 718 and 772mg PH_3/g respectively. The former was impregnated with 3% sodium dichromate and the latter with 0.01% silver nitrate.

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Table 8

WATER ADSORPTION RATE AND CAPACITY OF OVEN DRIED ACTIVATED CARBONS AND METAL OXIDES WITH TIME

ADSORBENT\HOURS	ADSORPTION (WEIGHT %)						
	24	72	96	168	260	352
ANDERSON 21	23.0	23.1	24.6	32.7	43.0	48.9
ANDERSON 31C	1.6	8.0	7.9	19.3	34.1	48.8
ANDERSON 31M	9.3	7.7	25.1	37.4	47.7	49.2
CALGON	3.9	17.7	15.7	17.3	24 2	27.6
MnO2	9.0	12.5	12.3	9 7	18.9	22.7
CuO	0.0	0.0	0.1	0.2	0.2	0.2

Table 9
PHOSPHINE CAPACITY OF OVEN DRIED SORBENTS

SORBENT	WEIGHT (mg)	PH$_3$ SORBED IN 96 HRS (mg)	PH$_3$ CAPACITY mg PH$_3$/g SORBENT
ANDERSON 21	6.7	6.62	>988
ANDERSON 31 C	9.2	4.37	475
ANDERSON 31 M	17.5	6.43	367
CALGON	5.9	5.77	978
SUTCLIFFE (Cr$_2$ O$_7$)	8.8	6.32	718
SUTCLIFFE (Ag)	6.0	4.63	772
Mn O$_2$	8.7	6.43	739
CU O	29.0	6.63	228
MnO$_2$/Cu O			
10/0	10.3	6.29	611
8/1	11.3	6.55	580
6/1	6.8	4.63	681
4/1	9.6	4.03	420
2/1	11.6	2.09	180
1/1	14.2	4.05	287

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MnO_2 and CuO gave capacities of 732 and 228 mg PH_3/g respectively. None of the six mixtures investigated were greater than MnO_2 alone.

3.7.2 Moist Sorbents.

The water adsorbed by the AC's as a function of time are shown in Table 8. At 352 hours, the Anderson-AC's were about 49% water, Calgon 27.6%, MnO_2 22.7% and CuO 0.2%.

It was decided to repeat the PH_3 capacity for some of the sorbents as they were received from the manufacturers. The quantity of sorbent used, the amount of PH_3 sorbed in 96 hours and the PH_3 capacity are given in Table 10.

3.7.3 PH_3 Capacity from Moist and Dry Sorbents.

In Table 11 are given the PH_3 capacity of AC's as received (moist) and after drying. With the exception of Anderson-21 and Calgon, the moist AC's gave PH_3 capacity greater than the corresponding dry ones. This may be feasible if the PH_3 reacts with the moisture to form phosphorus acids and also being sorbed by AC.

4. DISCUSSION

The amount of water vapor in a given volume of air is a function of temperature and pressure[5]. Given these parameters, the weight of the water may be calculated from the gas law:

$$g = pvM/RT$$

The weight of water vapor in 1 liter of air as a function of temperature and vapor pressure has been calculated and the results are given in Table 12. The normal RP munition's storage temperature may be 20-70°C which corresponds to 1.73-19.63 mg water vapor. The upper limit should be the basis for determining the amount of desiccant needed for drying the interior of a RP munition round.

If it were decided to use Al-Si-Clay to remove 19.63mg water, by using the water capacity value from Table 1 of this desiccant, it would require 0.080g Al-Si-Clay. This desiccant, known as Desi-Pak contains 4.4g of dry Al-Si-Clay which is 55 times more than is required. Silica gel and molecular sieves could also be used but they are slightly less efficient. Calcium sulfate is the least efficient of all with a water capacity of 7%. The remaining metal salts have to be avoided; because after a certain time of water exposure they deliquesce.

Table 10

PHOSPHINE CAPACITY OF SORBENTS AS RECEIVED FROM MANUFACTURER

SORBENT	WEIGHT (mg)	PH3 SORBERD IN 96 HRS, (mg)	PH3 CAPACITY mg PH3 / g SORBENT
ANDERSON 21	8.3	6.62	798
ANDERSON 31C	7.0	6.36	909
ANDERSON 31M	13.3	6.62	498
CALGON	9.3	6.62	712
SUTCLIFFE (DICHROMATE)	6.4	6.50	1034
SUTCLIFFE (SILVER)	6.9	6.62	959
MnO2	8.0	6.62	825

Table 11
PHOSPHINE CAPACITY OF SORBENTS AS RECEIVED AND AFTER DRYING

SORBENT	AS RECEIVED		DRY CAPACITY	Δ CAPACITY $(C_M - C_D)$
	% WATER	CAPACITY		
ANDERSON 21	62.4	798	>988	-190
ANDERSON 31C	0.6	909	475	434
ANDERSON 31M	3.1	498	367	131
CALGON	0.9	712	978	-266
SUTCLIFFE (Cr$_2$O$_7$)	13.2	1034	718	316
SUTCLIFFE (Ag)	11.8	959	772	187
Mn O$_2$	25.0*	828	739	81

* ADDED SUFFICIENT WATER TO EQUAL 25%

The evolution of PH_3 from RP is a function of RH, time and temperature. This is illustrated by the results for ERCO's RAP in Table 3. In order to stop PH_3 evolution, the RP must be protected from a moist atmosphere. This can be accomplished by the use of a desiccant and having an air tight system.

Stabilization of RP slows down the PH_3 evolution but it does not stop it. It is just a matter of time that eventually sufficient PH_3 will build up to cause a corrosive condition. The stabilized RP's (HB100S and RAPS) when compared with raw RAP at 85% RH are 29.3-114.5 times more stable. When carried out in dry nitrogen and silica gel, the stabilized RP's are only 1.6-6.9 times more stable. Careful inspection of the data in Table 4 reveals that a dry condition contributes more to RP stability than the stabilized counterpart.

The effect of water and AC on RAP at room temperature is given in Table 5. The presence of water vapor, as it is well known, accelerates the formation of PH_3. The presence of AC indicated no PH_3 in the reaction chamber, but what actually happened in this case was that the PH_3 was sorbed as it was formed. The presence of water and AC gave a negligible amount of PH_3. The significance of this is that AC is capable to sorb PH_3 in dry as well as in moist environment.

Desiccants and sorbents (Table 1) were both subjected to rate study with PH_3 with the anticipation of finding a desiccant which might interact with both water and PH_3. Results indicated that metal salts and molecular sieves reacted very slowly with PH_3. The metal oxides and AC's were relatively much faster. Mixtures of MnO_2 and CuO gave rates which were slower than MnO_2 alone. So the alleged mixture, 6:1, of these oxides was not supported by our results.

Among the AC's whose half lives ranged from 6.4-173 min; Anderson-21 was the most reactive, $t1/2=6.4$ min. The form or shape of the AC has a large influence on the reactivity. The order of reactivity based on shape was as:

powder > granules > pellets

which seems also to be directly related to the surface area of the AC.

The AC's received from Anderson, Calgon and Sutcliffe Speakman contained different amounts of water (Table 7). Before doing any measurements with them, they were dried. Then portions of the dry carbons were exposed to water vapor for 352 hours, at which time the water capacities were 22.7-49.2%. MnO_2 and CuO were also exposed to water vapor: MnO_2 had a water capacity to 22.7 and CuO had 0.2% (see Table 8). From these results, it might seem possible that AC's might be able to serve a double role: adsorb water and sorb PH_3 simultaneously.

The capacity of PH_3 was determined using dry (Table 9) and moist sorbents (Table 10). With the exception of Anderson-21 and Calgon, the sorbents had a greater capacity than when dry (see Table 11). It may be possible that two phenomena are occurring with the moist sorbents: the PH_3 is sorbed by water displacement and in turn the displaced water reacts with other PH_3 molecules which could account for the higher PH_3 capacities.

Anderson-21 as received had a water capacity of 62.4% and its PH_3 capacity was 798 mg/g. The adsorption of water by AC is reversible, it can be easily removed by heating at 200°C. The sorption of PH_3 occurs by chemisorption which accounts for its irreversibility. The PH_3 is not removed by heating at 200°C.

Since the attractive forces between AC and PH_3 are much stronger than those of AC and H_2O, PH_3 can replace H_2O by the following displacement reaction:

$$AC --- H_2O + PH_3 ----> H_2O + AC(PH_3)$$
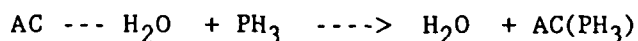
If the above displacement were to occur in a confined environment, the ambient moisture would increase. So it is necessary that the desiccant and sorbent used are thoroughly dry in order to prevent the above reaction from occurring.

How much desiccant should be used to dry up the free space of a RP munition round? Suppose that the free space were 1 liter and the temperature were 70°C or 160°F, then the water that needs to be removed is 19.63mg (see Table 12). If Al-Si-Clay is used whose capacity was found to be 25%, then the weight of this desiccant required is 80mg. The commercially available Desi-Pak (3x3x1/8", containing 4.4g Al-Si-Clay) has 55 times more desiccant than would be required.

5.   CONCLUSION

A reaction chamber technique was developed which permitted the study of PH_3 evolution from red RP and sorption of PH_3 by sorbents under several environmental conditions.

Out of several desiccants and sorbents evaluated, Al-Si-Clay had the largest water capacity, and Anderson-21 had the best phosphine capacity.

A dual combination of Al-Si-Clay and an activated dry carbon will assure a corrosion free environment for RP munition provided the munition chamber is airtight.

Table 12
WEIGHT OF ONE LITER WATER VAPOR AT DIFFERENT TEMPERATURES

t (°C)	VAPOR PRESSURE (mm Hg)	WEIGHT OF WATER VAPOR/LITER** (mg)
0	4.58	0.48
10	9.21	0.95
20	17.54	1.73
30	31.82	3.03
40	55.32	5.09
50	92.51	8.28
60	159.38	13.83
70	233.7	19.63
80	355.1	29.93
90	525.8	41.87
100	760	58.81

* F. DANIELS "OUTLINES OF PHYSICAL CHANGE" (1948) p 171

** $g = \dfrac{pv \, M}{RT}$

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A perfectly sealed munition chamber should have more priority than stabilized RP.

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